PINE BARK AS A TRICKLING FILTER MEDIA TO PURIFY WASTE WATER STREAMS FROM A KRAFT PULP AND PAPER MILL

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

By

John William Mitchell, Jr.

In Partial Fulfillment

of the Requirement for the Degree

Master of Science in Mechanical Engineering

Georgia Institute of Technology

August, 1975

PINE BARK AS A TRICKLING FILTER MEDIA TO PURIFY WASTE WATER STREAMS FROM A KRAFT PULP AND PAPER MILL

Approved:

George R. Lightsey, Chairman

William Z. Black

Gene T. Colwell

Date approved by Chairman: July 14, 1975

ACKNOWLEDGMENTS

To Dr. George R. Lightsey, whose enthusiasm and guidance played a major role in this work.

To Dr. William Z. Black, who inspires one to seek knowledge, and Dr. P. Durbetaki for his encouragement.

To Dr. G. T. Colwell for serving as a member of the thesis reading committee and his helpful advice.

To John Travis for his contribution to the primary sludge project.

To Union Camp Corporation, Georgia Kraft Company, Scott Paper Company, and Buckeye Cellulose Corporation, for their material and laboratory contributions.

Finally, to Lillian, Jim, Mike, Bob, and Jeff.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

Waste water treatment methods are of considerable importance to the pulp and paper industry from both an economical and environmental position. Pine bark, an abundant manufacturing residue, is examined for its effectiveness as a trickling filter media and subsequently as a soil amendment.

Nine trickling filter models were examined for their ability to remove biochemical oxygen demand (BOD), chemical oxygen demand (COD), sodium, settleable matter, and color from a bleach plant waste water stream and a primary sludge stream from a clarifier. Conductivity and pH observations were recorded.

Results indicate that pine bark as a filter media is very effective in removing settleable matter from a primary sludge and BOD from the liquid fraction. The settleable matter presents itself as a dewatered sludge at the filter face and BOD removal in the liquid is up to 90 percent.

Experimental observations show that the BOD and COD removal efficiencies do not change significantly after the liquid has passed through approximately three feet of the bark media.

Collation of results suggests an optimum dosing rate of 9.20 gals., ft^{-2}, day^{-1} for maximizing BOD and COD removal and minimizing filter size. Maximum BOD and COD removal was 90 and 40 percent, respectively.

Observed values indicate significant amounts of sodium and color

are removed when a kraft bleach plant waste water is passed through a filter model with a composted bark as the media.

The nitrogen content of the pine bark media significantly increases after approximately two months use as a filter media.

CHAPTER I

INTRODUCTION

To establish and maintain a cleaner environment for mankind, there are laws, rules, and regulations, enforced by federal, state, and local governmental agencies. These regulations require that waste waters, solid waste residuals, and other wastes generated by man's activities be treated and/or controlled by methods that substantially reduce the probability of contaminating a receiving body.

Pulp and paper manufacturing is one of the major industries in the United States. The kraft process, centered in the southeast, accounts for 78 percent of all chemical pulp produced in this country (1). There are 11 kraft pulp mills located in Georgia, which is the largest pulp and paper producing state in the nation.

Kraft pulp and paper mills have historically used large volumes of fresh water in processing the wood fiber into pulp and paper. Water volumes used range from 12,000 to 52,000 gallons of fresh water per ton of air dried pulp produced (1). This fresh water, as it passes through the process, becomes contaminated with chemicals, cellulosic fibers, and other materials that are not captured in the chemical and physical recovery stages, but remain in the water.

Two contaminated waste water streams that are found in a kraft pulp mill are a sludge discharged from the primary clarifer and waste water from the bleach plant. For economical disposal, the sludge must be dewatered. The liquid fraction in the sludge and the bleach plant waste water must receive further biological, chemical, and physical treatment if 1985 proposed federal water quality emission standards are met.

Bark is an abundant solid waste residue of pulp and paper manufacturing. Approximately 15 percent of the total weight of the tree trunks cut in the forest is represented by bark (2). In a chemical pulping process about half of the wood weight to the digester is dissolved in the cooking liquor and pulp yield is 50 percent or less (3). A "typical" mill with the production capacity of 1000 tons per day of air dried pulp would generate approximately 300 tons of bark a day. Utilization and/or marketing of these quantities of bark can present a serious waste disposal problem to individual mills (4).

The primary objective of this research project was to couple the utilization of pine bark as a trickling filter media with the effectiveness of purifying and dewatering a primary sludge from a first stage clarifier and purifying waste water from a bleach plant. The effectiveness of purification and dewatering was determined by measurement of the biochemical oxygen demand (BOD), chemical oxygen demand (COD), sodium, settleable matter, color, pH, and conductivity of the waste water influents and the filtrates under observation.

Attempts to use bark as a trickling filter media with sewage effluents have been reported (5,6). It was found that bark was a good trickling filter media, reducing the levels of dissolved BOD and nutrients in the sewage effluent to very low levels. While bark itself has a nitrogen deficiency when used as an agricultural aid (5), after two and one-half months as a trickling filter media the bark's nitrogen concentration had been increased from about 0.2 percent to 0.49 to 0.67 percent (6).

Douglas fir bark as a trickling filter media for animal waste disposal systems has also been investigated (7). Test results show significant reduction of turbidity (JTU), and total solids as well as BOD, indicating its ability to effectively filter insoluble solids from waste water.

Treatment of a prehydrolysate waste water stream from a kraft mill using pine bark as a trickling filter media was investigated by Lightsey (8,9). During three months operation liquid samples collected from beneath the bark trickling filter showed a reduction in BOD of 80-85 percent, a reduction in color of 20-30 percent, and a reduction in sodium content of 50 percent. Only traces of nitrogen and phosphorous were found in the seepage or run-off water from under the bark piles, indicating that these nutrients were remaining with the bark.

Studies have shown (13) that sludge-bark mixtures can be economically utilized as a soil amendment if the nutrient content of the mixture is high. Bark that has been used as a trickling-filter media to dewater sludge would be expected to have a high nutrient content.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Instrumentation

The instruments used for the measurement of influent and filtrate color, electrical resistivity, pH, and sodium are listed below.

Color

Light transmittance and absorbance was measured with a photometer as manufactured by Bausch and Lomb, Spectronic 70, catalog number 33-30-74.

Electrical Resistivity

Electrical resistance was measured with a conductivity bridge as manufactured by Industrial Instruments, Inc., model number R C 16.

pH

Hydrogen ion concentration was measured with a pH meter as manufactured by Beckman Instruments, Inc., model number 96.

Sodium

Sodium ion concentration measurements were taken utilizing a specific sodium electrode, catalog number 13-639-20P, and a standard calomel reference electrode in conjunction with a pH/ion meter, model 230. Both instrument and electrodes were manufactured by Fisher Scientific Company.

Equipment

The equipment used to simulate the low rate trickling filter models for the primary sludge project is shown in Figure 1. Equipment used for the bleach plant waste water project is similar except a four inch round tube was used as the bark retaining structure. The wooden framework was constructed to accommodate six tubes.

Equipment and/or apparatus used in the measurement of BOD, COD, and suspended matter of the filter influents and filtrates are as listed below.

Biochemical Oxygen Demand

The equipment used to perform five-day biochemical oxygen demand (BOD) tests are as those listed in Standard Methods, 13th edition, page 489, 2. Apparatus.

Chemical Oxygen Demand

The equipment used to perform chemical oxygen demand (COD) tests are as those listed in Standard Methods, 13th edition, page 496, 2. Apparatus.

Settleable Matter

The equipment used to measure the suspended matter in a sample is as that listed in Standard Methods, 13th edition, page 537, 2. Apparatus.

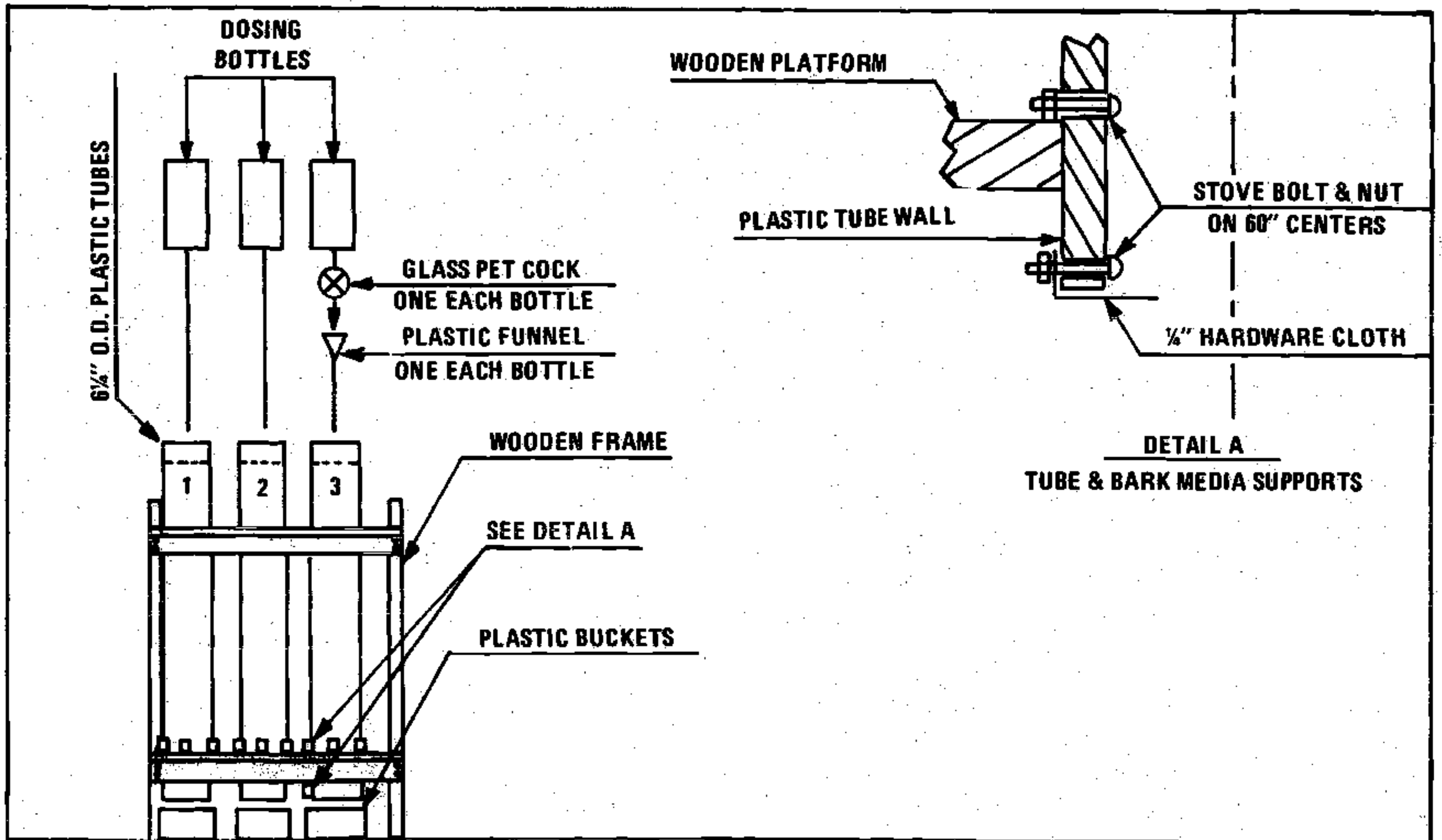

Figure 1. Arrangement of Trickling Filter Models, Primary Sludge Project

CHAPTER III

PROCEDURES

Operational Procedures

Primary Sludge Project

The primary sludge under examination was recomposed from a kraft pulp and paper mill primary clarifier bottom sludge that had been dewatered (30 percent solids by weight) and shipped to Georgia Tech in sealed containers.

The pine bark used in this project was collected at random from a belt conveyor transporting the bark from the debarking process within a kraft pulp mill. The bark fragments contained both inner and outer bark. These random bark samples were loaded into containers, sealed, and shipped to Georgia Tech. Random samples were taken from these containers to fill each tube to a depth of six feet.

Dewatered sludge, drinking water, nutrients, and sulfuric acid were mixed and mechanically agitated daily to recompose the primary sludge. This solution had an average solids concentration of 3.5 percent by weight. The sulfuric acid was used to adjust the pH between six and nine. Nitrogen and phosphorous were added to the solution in the proportion of 12.5 and 2.5 milligrams of nutrient per liter of solution, respectively. This gave a nominal ratio of N : P : B.O.D. of 5 : 1 : 100.

This recomposed primary sludge was applied daily to each of the three filter models. Hydraulic loading rates were as shown in Table 1.

Table 1. Filter Model Designation and Parameters

Filter Number	Hydraulic Loading Rates (gals., ft^{-2}, day^{-1})
Primary Sludge	
1	1.15
2	2.30
3	4.59
Bleach Plant Waste Water	
4	3.10
5	9.20
6	18.4
7	36.8
8	18.4
Bleach Plant Waste Water and Composted Bark Media	
9	9.20

These rates were established by dosing filters number one, two, and three with 850, 1700, and 3410 milliliters, respectively, of influent each day.

Difficulty was experienced with the plugging of the one quarter inch plastic tubing lines from the dosing bottles to the filters. This problem was attributed to the lack of good fibrous particle separation when recomposing the dewatered sludge and equipment size limitations with a laboratory model. This difficulty was circumvented by manual application of the sludge to each filter.

Blinding of the filter face, by the accumulation of fibrous solids, became so severe after several days that passage of the liquid fraction to the filter media was interrupted. Liquid flow was maintained by periodically removing the collected solids.

<u>Bleach Plant Waste Water Project</u>

Waste water from a kraft pulp mill bleach plant was shipped to Georgia Tech in sealed 55 gallon containers. One shipment of two containers was received two days before this project started. The final shipment of two containers was received 58 days after start-up of this project and application to filters began on the 59th day.

Containers were stored at ambient room conditions. Care was taken to keep containers sealed except when in use. Shipments were made at intervals and containers kept sealed to minimize the change in chemical and biological composition.

The pine bark filter media came from the same source as that used in the primary sludge project. Filter models were filled with bark to a depth of six feet.

During the application of liquid from the first container, waste water and nutrients were mixed with the waste water daily. Nitrogen and phosphorous were added to the solution in the proportion of 12.5 and 2.5 milligrams of nutrient per liter of solution, respectively, giving a nominal N : P : B.O.D. ratio of 5 : 1 : 100. This bleach plant waste water influent was applied daily to each filter model under observation. Hydraulic loading rates were as shown in Table 1. These rates were established by dosing filters number four, five, six, and seven with 1150, 3440, 6880, and 13,760 milliliters, respectively, of influent each day. Filter number eight was dosed with a mixture of 3440 milliliters of influent and 3440 milliliters of recycled filtrate each day. Filter number nine was a special project and is discussed in Chapter IV.

During the application of liquid from the second container a change was made in the operational procedure. The waste water influent was applied to the filter media only on the days that measurements were to be taken. On other days, the filtrate was recycled through the media.

The liquid from the third container was applied as that from the first container. No liquid was applied on Saturday or Sunday during application of the contents from the fourth container.

Test Procedures

BOD

Five-day biochemical oxygen demand tests were conducted essentially as stated in Standard Methods, 13th edition, pp. 489-495 (10). Three hundred (300) milliliter incubation bottles were used for the tests.

No seed was introduced into the sample to be incubated. All filtrates contained sufficient initial microbial population to oxidize the biodegradable fraction of the organic matter in the waste water under observation.

COD

Chemical oxygen demand tests were performed essentially as stated in Standard Methods, 13th edition, pp. 495-499. Sulfuric acid reagent was prepared using 24 grams of silver nitrate per nine pound bottle of acid in lieu of 22 grams of silver sulfate.

Color

The term "color" is used herein to mean "true color." True color is the color of the liquid under observation from which the turbidity has been removed.

The procedures used to measure color were essentially as described in the National Council of the Paper Industry for Air and Stream Improvement, Incorporated, Technical Bulletin Number 253. An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color (11).

The pH of the sample was adjusted to 7.6 after it had passed through an 0.8 micron porosity membrane filter. It was found that the pH increased approximately 0.6 if the sample was adjusted to 7.6 pH prior to filtering, as the procedure in bulletin 253 suggests.

A calibration curve was obtained by plotting observed photometric absorbance values against color standards. These color standards were prepared by diluting a potassium chloroplatinate standard solution with distilled water. The curve is presented in Figure 12 in the Appendix.

Electrical Resistivity

Electrical resistance of the liquid sample under observation was measured with a conductivity bridge. The cell constant factor was determined by measuring three known conductance values for three molar concentration of potassium chloride as shown in Standard Methods, 13th edition, p. 325. An arithmetic mean cell constant of 0.136 and the measured instrument reading were used to calculate the specific conductance of these liquids. The variance (σ^2) of the cell constant determination was 2×10^{-6}.

Sodium

A sodium ion-selective electrode and a standard calomel reference electrode in conjunction with a pH/ion meter were used to measure the ionic activity of the sodium ion in the liquid solution under test. Sodium ion concentration was determined by precalibrating the electrodes with standard sodium ion solutions of known concentrations.

To construct the calibration curve a 10 molar standard solution of sodium chloride using distilled water was prepared. This stock solution was subsequently diluted into five sample solutions with fiftyfold changes in concentration (5000 PPM to 100 PPM). The measured millivolt potential of each sample concentration was recorded and the results plotted on semi-log graph paper. The pattern of these results is shown in Figure 13 in the Appendix.

Complete operational instructions are described by Instructions E-15, Sodium Ion, published by Fisher Scientific Company (12).

Nitrogen Concentration

Nitrogen concentration of the pine bark was determined by the Total Kjeldahl method as described in Standard Methods, 13th edition, page 469.

pH

A Beckman pH meter was used for measuring the hydrogen ion concentration. Temperature compensation was by manual control. The meter was standardized frequently with a 7.0 buffer solution.

Settleable Matter

This test was done as described in Standard Methods, 13th edition, page 539.

CHAPTER IV

RESULTS

BOD and COD Sample Data

Observed concentrations of BOD and COD in the influents and filtrates for the time interval that the three primary sludge filters were under examination are shown in Table 12 in the Appendix. The data for the five bleach plant waste water filters are recorded in Table 13 in the Appendix.

BOD and COD Performance Patterns

The ability of each filter model to remove BOD and COD from the influents is exhibited in this chapter with behavioral patterns. These patterns were generated by using a least squares method to obtain the best fit to the observed data points. The polynomial coefficients, variances, and standard deviations are given in Table 14 in the Appendix.

Primary Sludge Project

Filter Number 1

BOD concentrations, as observed in the filtrate nine days after dosing started, were higher than the averaged influent concentrations. Table 12 shows that after 23 days the BOD concentration in the filtrate had decreased to 65 mg, 1^{-1}, representing an 80 percent removal of BOD from the influent. At the end of 50 days operation, removal of BOD was approximately 95 percent, as indicated in Figure 2.

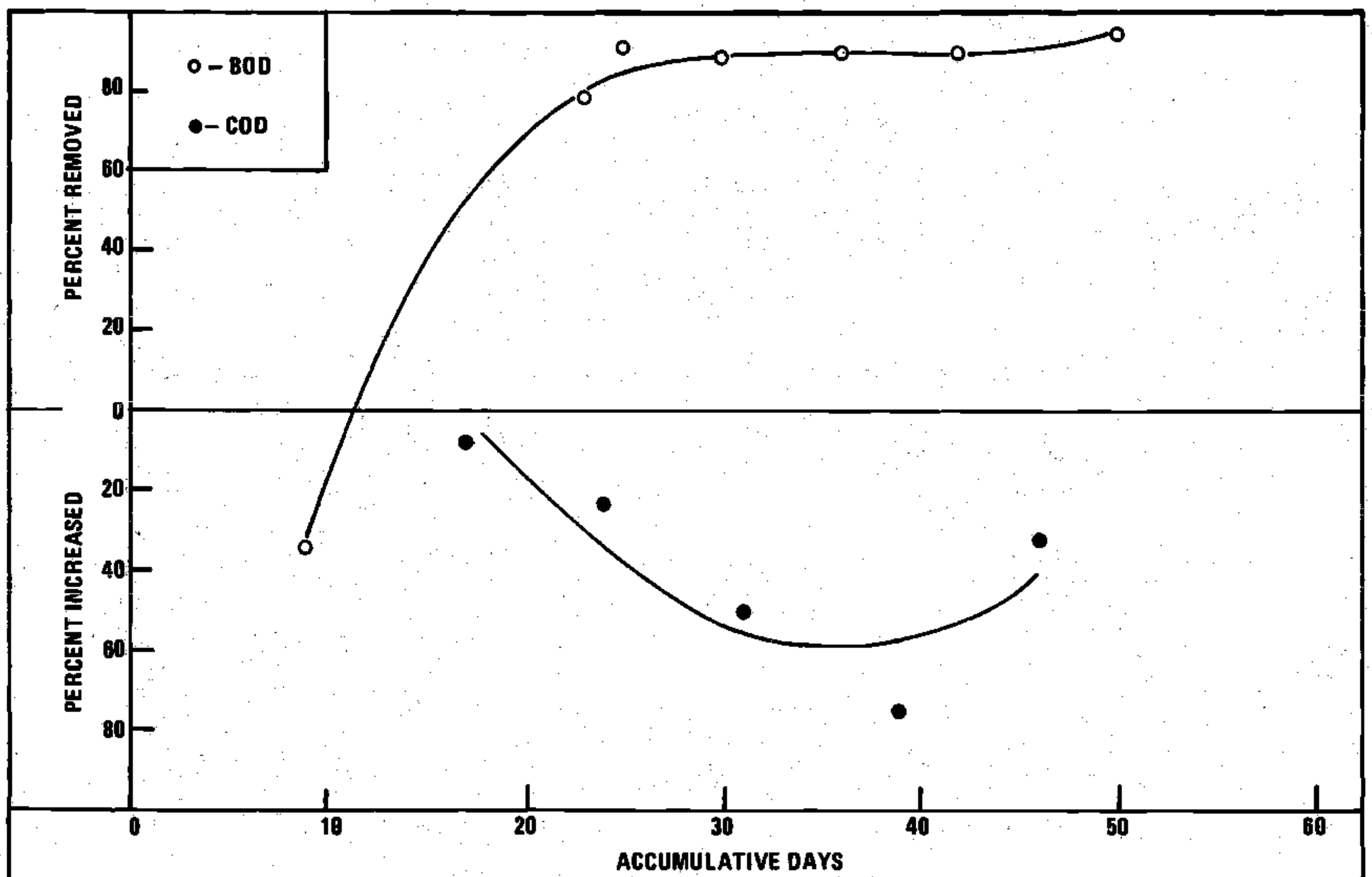

Figure 2. Effect of Time on the Performance of Filter Number 1

The concentration of COD in the filtrate increased with time for about 36 days and then began to decrease until the project was terminated on the 46th day. All measured concentrations of COD in the filtrates were higher than the averaged influent COD value.

Specific conductance of the filtrate was higher than the influent for every measurement taken. However, the ionic activity decreased with time as shown by collation of influent and filtrate values in Table 2. The highest specific conductance value of 14,200 μmhos, cm^{-1} was observed on the 14th day and the lowest value of 5900 μmhos, cm^{-1} was recorded on the 43rd day.

Sodium ion concentrations in the filtrate decreased by 16 and 23 percent for the two measurements taken near the termination of the project.

The change in pH after the influent passed through this filter was erratic with time. On two days the pH increased, decreased on two days, and remained unchanged on a 5th day.

On the 45th day there was a reduction in the number of color bodies in the filtrate. The color reduction was 31 percent using averaged measured chloroplatinate color units (CCU) for the influent.

Filter Number 2

Figure 3 reflects the ability of this model to remove BOD and COD from the influent with time.

BOD removal efficiency ranged from a low of 60 percent on the 9th day to a high of 95 percent at the termination of dosing on the 50th day.

The COD curve followed a pattern similar to model number 1. Concentration of COD in the filtrates increased initially. After approxi-

Table 2. Filter Number 1, Chemical and Physical Properties of Influents and Filtrates

	Σ Days	14	22	25	29	36	37	39	43	45
pH	Influent	7.1	6.6		6.7		8.0		7.7	
	Filter no. 1	6.6	6.6		7.1		7.8		8.3	
Specific Conductance (μmhos,cm^{-1})	Influent	7960	5400		3300	7300			4400	
	Filter no. 1	14200	13900		10900	7800			5900	
Sodium Ion (PPM)	Influent			740				800		
	Filter no. 1			620				620		
Color (CCU)	Influent	----*			---*		5400*		3600	3400
	Filter no. 1	1300*			950*		4500*		5280	4950

*Error in procedure.

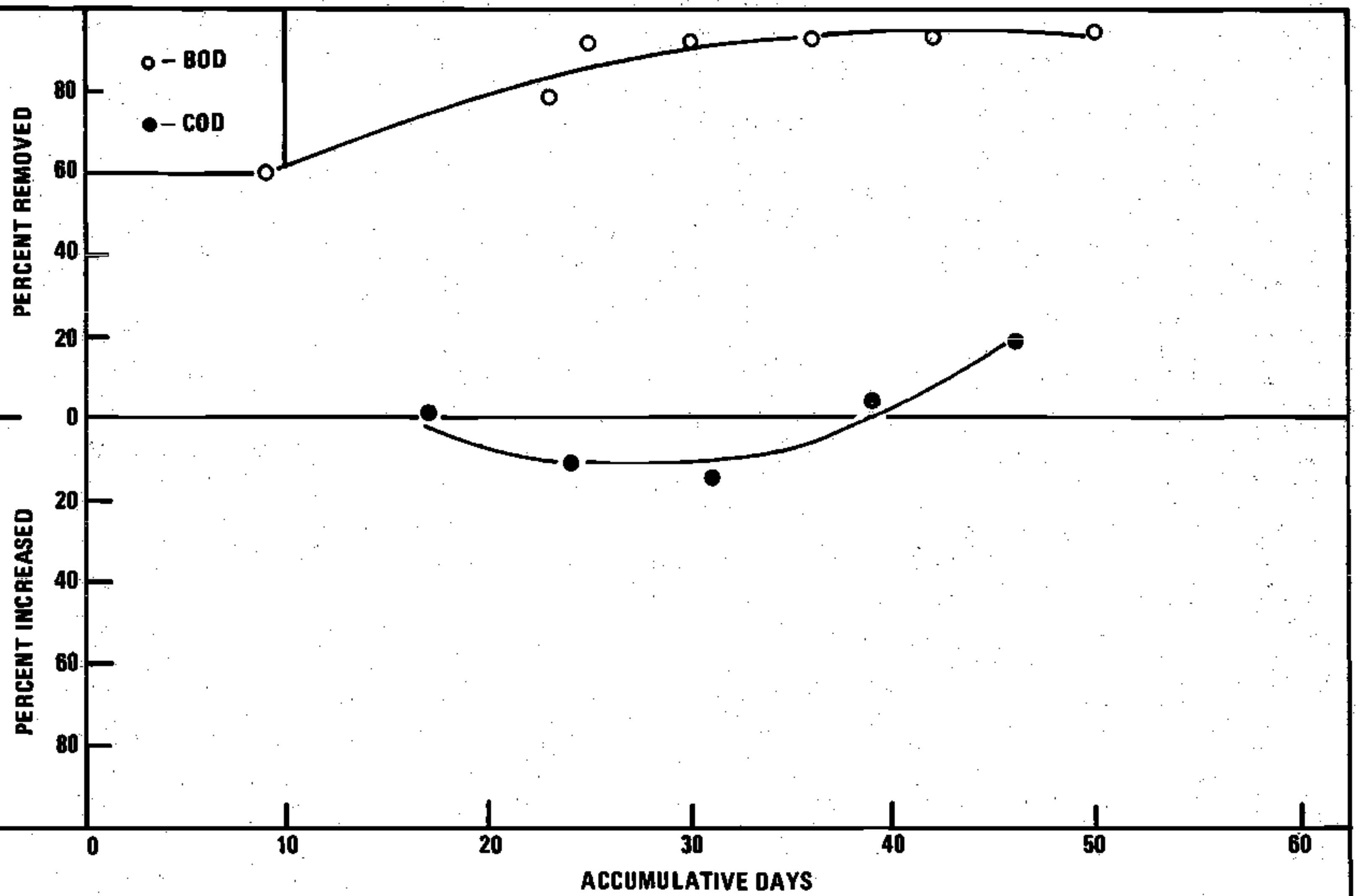

Figure 3. Effect of Time on the Performance of Filter Number 2

mately 30 days operation, the performance started to improve and on the 46th day the data reflect a 20 percent removal efficiency.

The chemical and physical properties used to characterize the influents and filtrates are shown in Table 3.

Changes in the specific conductance of the filtrate, with time, behaved similar to filter model number 1. The observed values ranged from 15,300 μmhos, cm^{-1} on the 8th day to 6000 μmhos, cm^{-1} on the 43rd day.

Sodium ion activity in the influent increased for the two data points taken on the 25th and 39th days. The averaged increase in activity was approximately 48 percent.

Collation of results shows that the hydrogen ion activity in the influent decreased for each observation taken between the 22nd and 43rd days. On the 14th day there was an increase.

Color bodies concentration in the influents was reduced by 14 and 18 percent for the values observed on the 43rd day and 45th day, respectively.

<u>Filter Number 3</u>

The BOD and COD removal performance of this model continuously increased during the time interval it was under observation as indicated in Figure 4.

BOD removal percents ranged from 70 percent on the 9th day to 95 percent on the 42nd day.

Removal of COD over the same time interval ranged from an initial low value of 14 percent to a high value of 42 percent at the project termination.

Table 3. Filter Number 2, Chemical and Physical Properties of Influents and Filtrates

	Σ Days	14	22	25	29	36	37	39	43	45
pH	Influent	7.1	6.6		6.7		8.0		7.7	
	Filter no. 2	7.0	8.2		8.2		8.6		8.7	
Specific Conductance (μmhos,cm^{-1})	Influent	7960	5400		3300	7300			4400	
	Filter no. 2	13300	9200		7000	6400			6000	
Sodium Ion (PPM)	Influent			740				800		
	Filter no. 2			1150				1130		
Color (CCU)	Influent	----*			----*		5400*		3600	3400
	Filter no. 2	1700*			1500*		2400*		3000	2860

*Error in procedure.

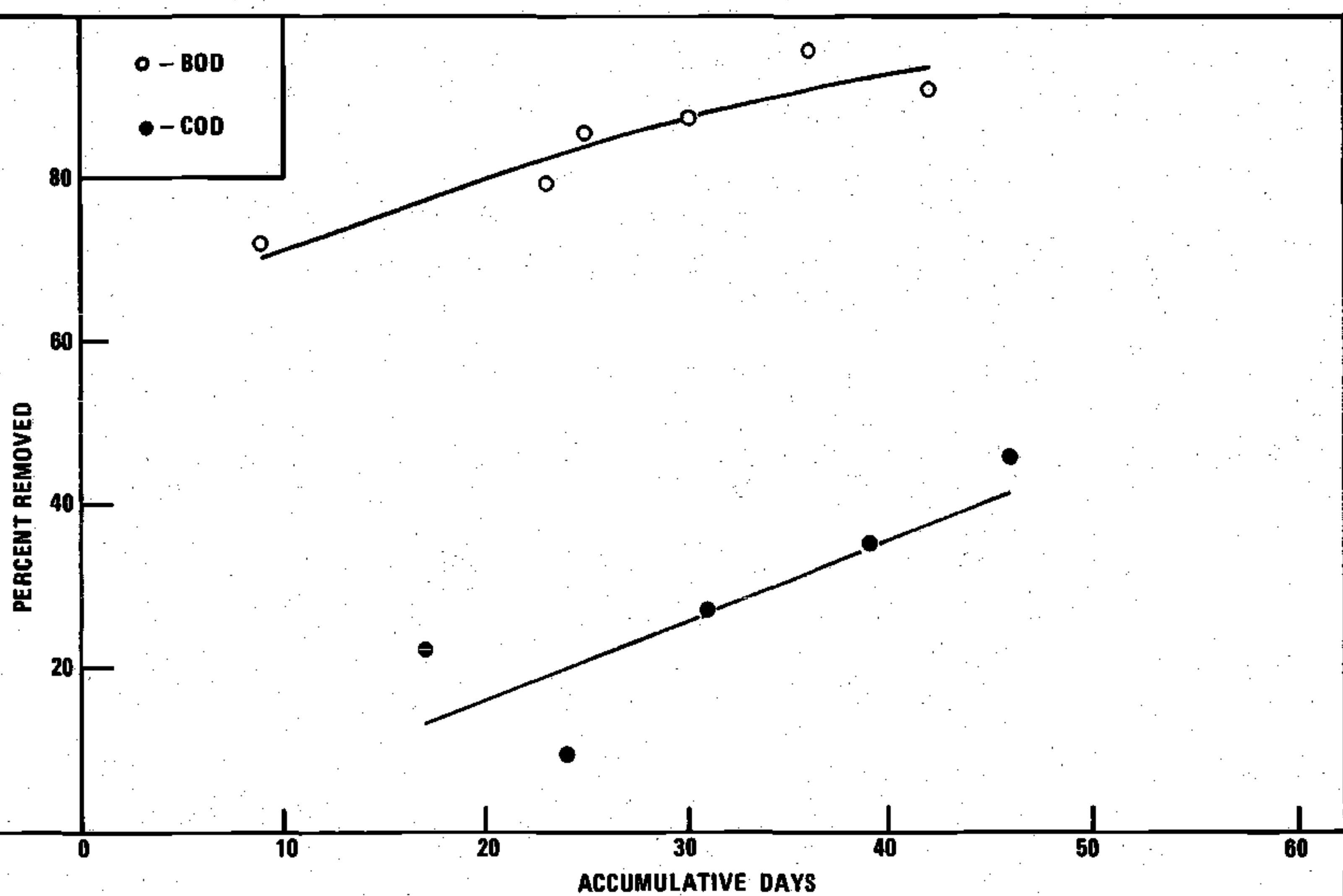

Figure 4. Effect of Time on the Performance of Filter Number 3

Measured values of the chemical and physical properties of the influent and filtrates are shown in Table 4.

Collation of data shows that the specific conductance of the filtrate was higher than the influent for four observations and lower for one observation on the 36th day. The ionic activity in the filtrate decreased from a high value of 12,300 μmhos, cm^{-1} on the 14th day, to 6100 μmhos, cm^{-1} on the 43rd day.

Sodium ion concentration in the filtrate was higher than the influent for the two data points taken on the 25th day and the 39th day. The averaged increase was 48 percent.

The pH of the influent increased with time for the duration of the project. The arithmetic means of the increase was a pH of 1.1.

The performance of this model indicates a removal of color bodies from the influent of 35 percent on the 43rd day and 55 percent on the 45th day.

<u>Settleable Matter</u>

Several settleable matter tests were performed on the filtrate from the three filter models. The highest value observed was 0.5 ml, 1^{-1} and most measurements showed only a trace of solids. Considering the influent had a concentration of 3.5 percent total solids by weight, with approximately 800 ml, 1^{-1} settleable matter, the percent removal of the settleable matter was 99 percent plus.

<u>Dewatering</u>

Three samples of sludge that had accumulated above the filter face were measured for solid and liquid mass fractions. The arithmetic mean value of these three samples was 17.7 percent solids and 82.3 percent

Table 4. Filter Number 3, Chemical and Physical Properties of Influents and Filtrates

	Σ Days	14	22	25	29	36	37	39	43	45
pH	Influent	7.1	6.6		6.7		8.0		7.7	
	Filtrate	7.8	8.3		8.2		8.6		8.5	
Specific Conductance (μmhos, cm^{-1})	Influent	7960	5400		3300	7300			4400	
	Filtrate	12300	8600		6200	5400			6100	
Sodium Ion (PPM)	Influent			740				800		
	Filtrate			1150				1130		
Color (CCU)	Influent	----*					5400*		3600	3400
	Filtrate	1520*					1950*		2250	1590

*Error in procedure.

liquid.

Bark Depth and Filter Performance

Each of the three filter models was subjected to BOD and COD performance measurements with bark depth. Depths selected were one foot, three feet, and six feet. The six foot depth data points were derived by taking averaged measured values of the influent and filtrate during the time period they were under observation. Figure 5 reflects the removal performance of BOD and COD from the influent with bark depth, for each of the hydraulic loading rates.

These curves indicate that the filter models with the two higher loading rates reach a maximum removal performance when the bark depth is three feet. BOD and COD filtrate data for the one foot and three foot depths are shown in Table 5.

Bark Media Nitrogen Concentration

At the end of fifty days operation random samples of bark media within each of the three tubes were collected from a bark depth < 3 feet and > 1 foot and the upper one foot section of the column. Bark media from the lower three foot column section was collected and combined from each of the three tubes to form a composite sample. The nitrogen analysis of these samples and the samples of the initial bark resulted in values that are plotted in Figure 6. The results indicate that the bark nitrogen concentration increases with increased hydraulic loading rates and with depth.

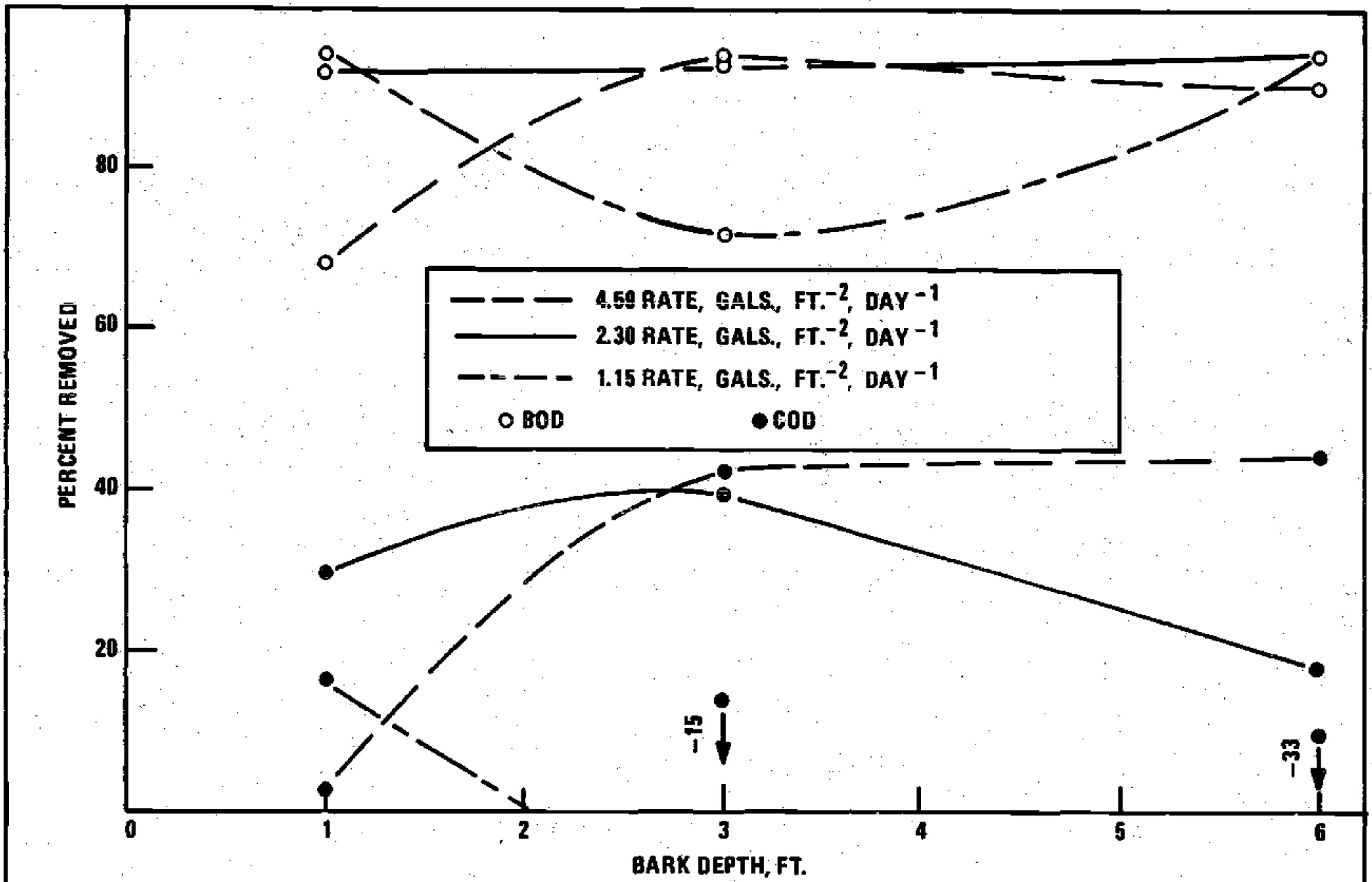

Figure 5. Effect of Bark Depth on Filter Performance

Table 5. Primary Sludge Project, BOD and COD Filtrate Data with Changes in Bark Depth and Hydraulic Loading Rates

Bark Depth	Hydraulic Loading Rate (gals., ft^{-2}, day^{-1})	BOD (mg, l^{-1})	COD (mg, l^{-1})
One Foot	1.15	18	808
	2.30	24	680
	4.59	96	940
Three Feet	1.15	300	961
	2.30	20	590
	4.59	18	560

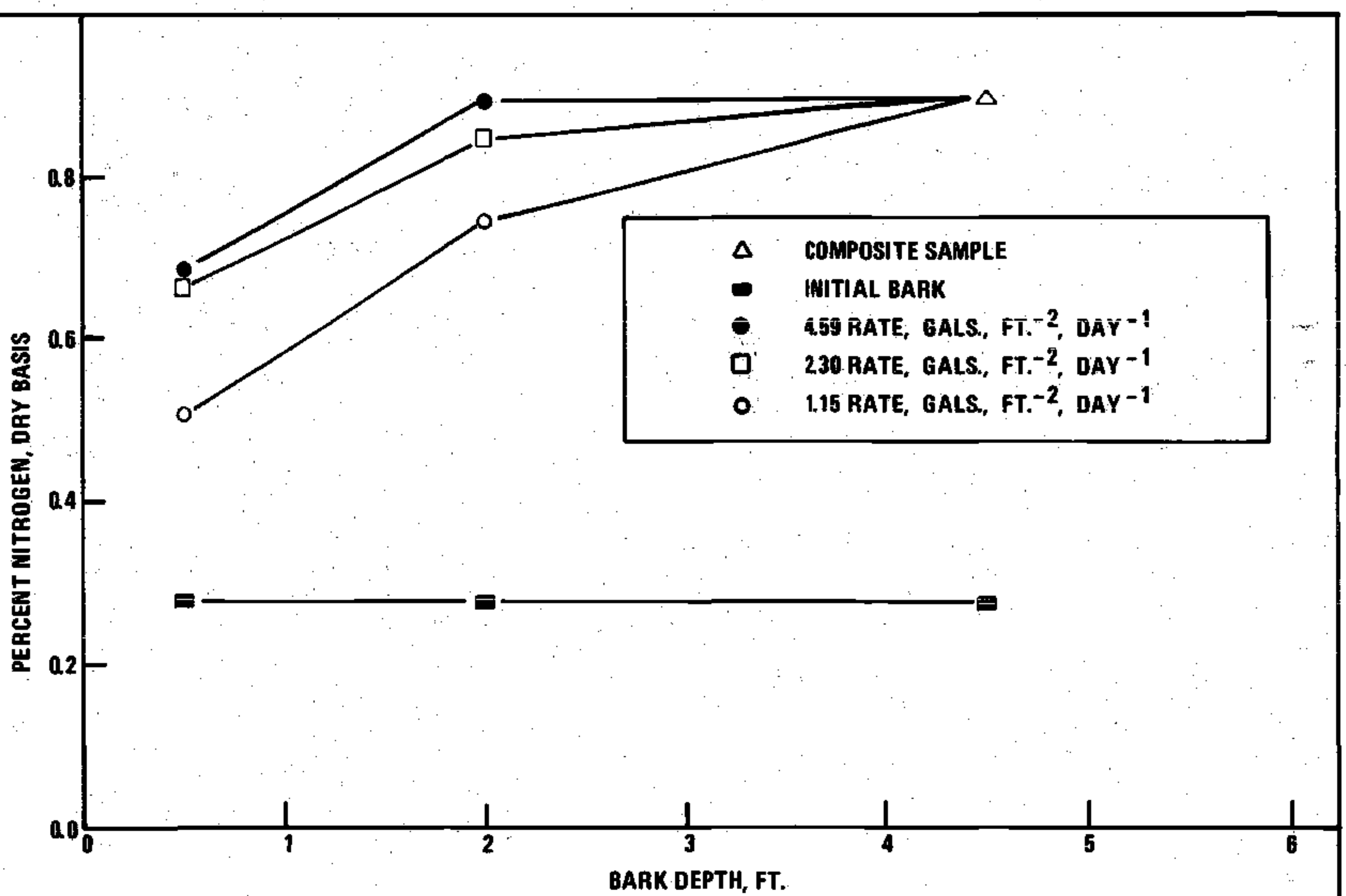

Figure 6. Effect of Bark Depth on the Nitrogen Concentration with Changes in Hydraulic Loading Rates

Bleach Plant Waste Water Project

Filter Number 4

Results of the BOD and COD removed from the influent with increasing time and a suspended dosing interval of 12 days are shown in Figure 7.

BOD removal percentages increased from 60 percent on the 9th day to approximately 95 percent on the 42nd day. Suspended dosing had little effect upon the removal performance of BOD.

COD removal increased with time from 10 percent on the 17th day to 24 percent on the 46th day. When dosing was suspended, the COD concentration of the filtrate was higher than the influent by approximately 65 percent, but after seven days of operation the behavioral pattern indicates that 55 percent of the COD in the influent was removed.

Observed chemical and physical characteristics of the influents and the filtrates are shown in Table 6.

The observed pH values of the filtrates were higher than the influent values except on the 25th day and 61st day.

The ionic activity in the filtrate decreased with time and on the 25th day, 29th day, and 43rd day the specific conductance of the filtrate was lower than the influent.

On the 25th day the sodium ion concentration in the influent was reduced by 20 percent.

Collation of results shows that color bodies in the filtrate were 8 and 23 percent less than in the influent on the 43rd day and 45th day, respectively.

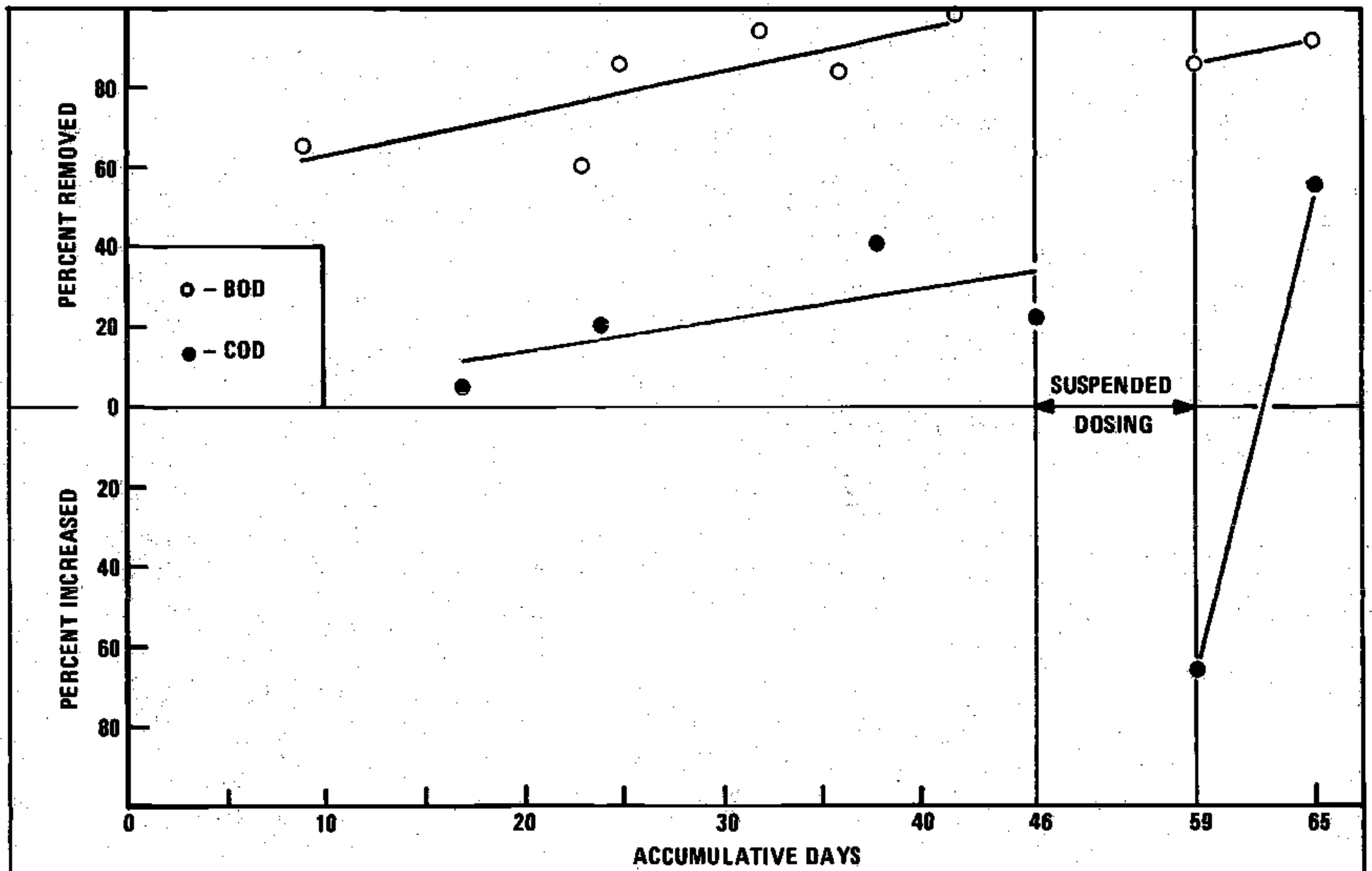

Figure 7. Effect of Time and Suspended Dosing on the Performance of Filter Number 4

Table 6. Filter Number 4, Chemical and Physical Properties of Influents and Filtrates

pH

Σ Days	8	14	22	25	29	37	43	46	61	65
Influent	6.5	7.2	6.5	8.4	7.1	7.7	7.9	7.6	7.6	7.0
Filtrate	6.7	7.3	7.6	7.7	7.7	7.9	8.0	8.0	6.9	7.2

Specific Conductance (μmhos, cm^{-1})

Σ Days	8	14	22	25	29	37	43	61	63	65
Influent	6300	6200	6500	6600	6300	6200	6500	4000	4000	3900
Filtrate	14800	8400	7500	5700	6200	6800	6300	5900	4900	4500

Sodium Ion (PPM)

Σ Days	25	38	59	61	63	65
Influent	1000	990	550	580	530	550
Filtrate	800	990	1000	990	780	690

Color (CCU)

Σ Days	8	15	29	37	43	45	59	61	63	65
Influent	1560*	1170*	1590*	1710*	1890	2790	900‡	1140	1140	1370
Filtrate	2400*	2250*	1890*	2160*	1740	1860	3080	2550	1940	1780

*Error in procedure.

‡Filtered twice through 0.8 μ membrane filter.

Filter Number 5

The performance patterns of BOD and COD removed from the influent with time and a suspended dosing interval are shown in Figure 8.

During the observed time interval from day nine to the 42nd day, the BOD removed from the influent shows progressively increasing values of 70 percent to 90 percent. After 12 days of suspended dosing, removal efficiency dropped to 80 percent. At the end of seven days operation, the filter performance was near an efficiency of 95 percent.

Concentrations of COD in the filtrate did not change significantly with time during the time interval that measurements were taken. The curve indicates a five percent decrease in removal efficiency in a time period of 17 to 46 days. Suspended dosing resulted in an increase in COD concentration in the filtrate on the day operation was resumed. In seven days the concentration of COD in the filtrate reflected a removal efficiency of 25 percent.

Observed properties of the influent and filtrate are shown in Table 7.

The hydrogen ion activity in the filtrate was less than the influent for seven out of the ten sample measurements.

The specific conductance of the filtrate was higher than the influent's except on the 25th day. The ionic activity of the filtrate decreased with time. The specific conductance was 12,300 μmhos, cm^{-1} on the 8th day and 41,000 μmhos, cm^{-1} on the 65th day.

Sodium concentration in the filtrate increased on the 59th day through the 65th day. On the 25th day and 38th day there was no change in sodium concentration.

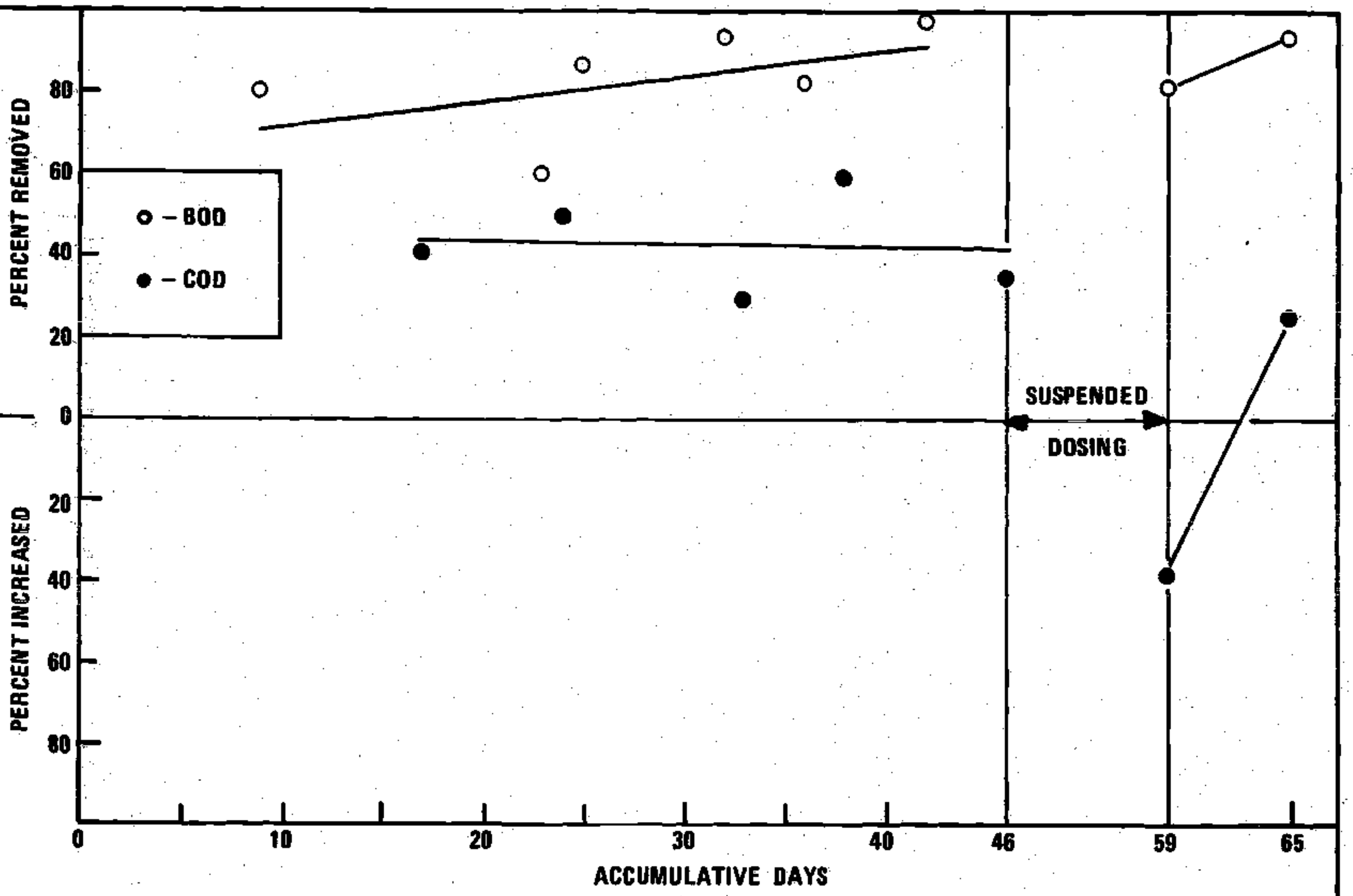

Figure 8. Effect of Time and Suspended Dosing on the Performance of Filter Number 5

Table 7. Filter Number 5, Chemical and Physical Properties of Influents and Filtrates

pH

Σ Days	8	14	22	25	29	37	43	46	61	65
Influent	6.5	7.2	6.5	8.4	7.1	7.7	7.9	7.6	7.6	7.0
Filtrate	6.9	7.5	7.6	7.6	7.6	7.9	8.0	7.9	7.3	7.8

Specific Conductance (μmhos, cm^{-1})

Σ Days	8	14	22	25	29	37	43	61	63	65
Influent	6300	6200	6500	6600	6300	6200	6500	4000	4000	3900
Filtrate	12300	6500	7200	6100	6500	6600	6500	4500	4200	4100

Sodium Ion (PPM)

Σ Days	25	38	59	61	63	65
Influent	1000	990	550	580	530	550
Filtrate	1000	990	870	690	670	710

Color (CCU)

Σ Days	8	15	29	37	43	45	59	61	63	65
Influent	1560*	1170*	1590*	1710*	1890	2790	900‡	1140	1140	1370
Filtrate	1400*	1590*	1560*	1520*	1560	1710	2940	1560	1190	1190

*Error in procedure.

‡Filtered twice through 0.8 μ membrane filter.

The concentration of color bodies in the filtrate decreased for three consecutive measurements and reflected decreases of 11, 17, and 39 percent.

Filter Number 6

The results of BOD and COD removal percents with time and suspended dosing are exhibited in Figure 9.

The BOD curve indicates that this model reached a maximum removal efficiency of 75 percent in 15 to 25 days and then retrogressed to almost 60 percent on the 46th day. After 12 days of suspended dosing the removal efficiency increased from the 60 percent termination level to near 65 percent on the first day of resumed operation. At the end of seven operational days the BOD removal efficiency had increased to about 90 percent.

Removal of COD from the influent was similar to models 4 and 5 with a minimum of 20 percent removed on the 17th day and a maximum of about 35 percent on the 38th day. The curve indicates a slight decline in removal efficiency by the 46th day. Suspended dosing resulted in a drop in removal efficiency to five percent, on the first day of resumed operation. But at the end of seven days, the removal efficiency was increased significantly above any previous value.

Measured values of the chemical and physical constituents in the influents and filtrates are shown in Table 8.

The pH of the filtrate tended to be slightly higher than the influent. However, on the 25th and 61st days the hydrogen ion activity of the filtrate increased.

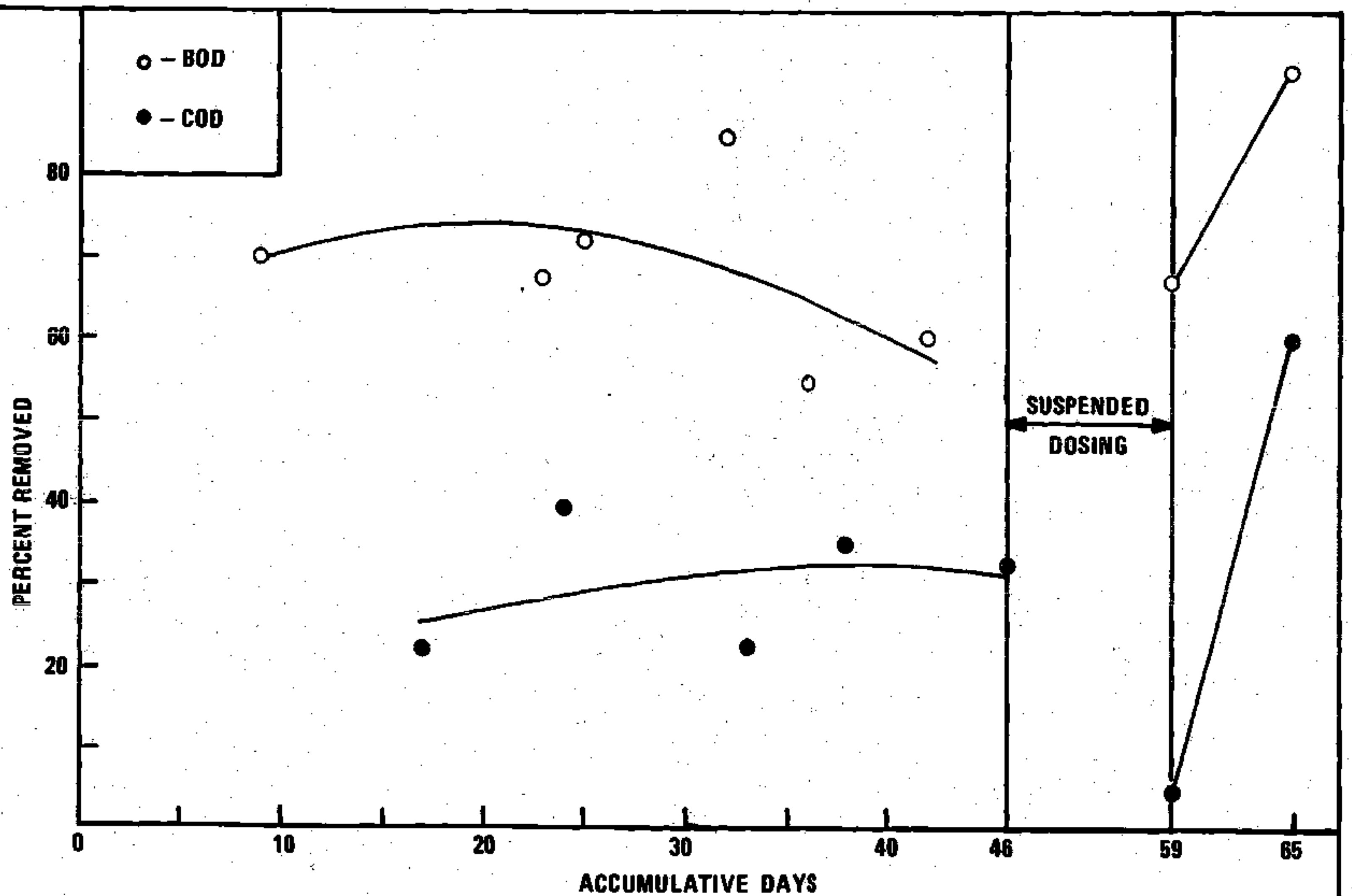

Figure 9. Effect of Time and Suspended Dosing on the Performance of Filter Number 6

Table 8. Filter Number 6, Chemical and Physical Properties of Influents and Filtrates

pH

Σ Days	8	14	22	25	29	37	43	46	61	65
Influent	6.5	7.2	6.5	8.4	7.1	7.7	7.9	7.6	7.6	7.0
Filtrate	7.0	7.6	7.6	7.2	7.6	7.9	7.9	7.8	7.4	7.5

Specific Conductance (μmhos, cm^{-1})

Σ Days	8	14	22	25	29	37	43	61	63	65
Influent	6300	6200	6500	6600	6300	6200	6500	4000	4000	3900
Filtrate	9700	6100	7000	6500	6500	6600	6200	4200	4000	3900

Sodium Ion (PPM)

Σ Days	25	38	59	61	63	65
Influent	1000	990	550	580	530	550
Filtrate	990	940	740	620	620	620

Color (CCU)

Σ Days	8	15	29	37	43	45	59	61	63	65
Influent	1560*	1170*	1590*	1710*	1890	2790	900‡	1140	1140	1370
Filtrate	1800*	1090*	1290*	1220*	1590	1740	1640	950	800	990

*Error in procedure.

‡Filtered twice through 0.8 μ membrane filter.

The specific conductance of the filtrate was lower than the influent for three of the ten measurements taken, higher for five, and two measurements showed no change. The ionic activity of the filtrate decreased from a high of 9700 μmhos, cm^{-1} on the 8th day to 3900 μmhos, cm^{-1} on the 65th day.

On the 25th day and 38th day, observed values of the sodium ion activity in the filtrate were slightly less than that of the influent. The four additional observations of this property show an increase in ion activity in the filtrate, all of which occurred after the 38th day.

This model manifested good color removal performance for the time periods from the 37th day through the 45th day and the 59th day through the 65th day. Removal efficiencies ranged from 15 to 40 percent.

Filter Number 7

Figure 10 exhibits the behavioral patterns of this filter's performance in removing BOD and COD from the influent.

On day one, concentration of BOD in the filtrate was 35 percent higher than the influent. On the 15th day, removal efficiency was 70 percent, and then retrogressed to a value of 45 percent on the 28th day.

COD removal experienced a logarithmic growth pattern starting on the first day of filter operation and continuing until approximately the 10th day at which time the curve pattern stabilized and remained at about 25 percent efficiency until the 28th day.

Measured values of the chemical and physical constituents in the influents and filtrates are shown in Table 9.

The pH of the filtrate was lower than the influent for all values recorded. The arithmetic mean of the differences is 0.4.

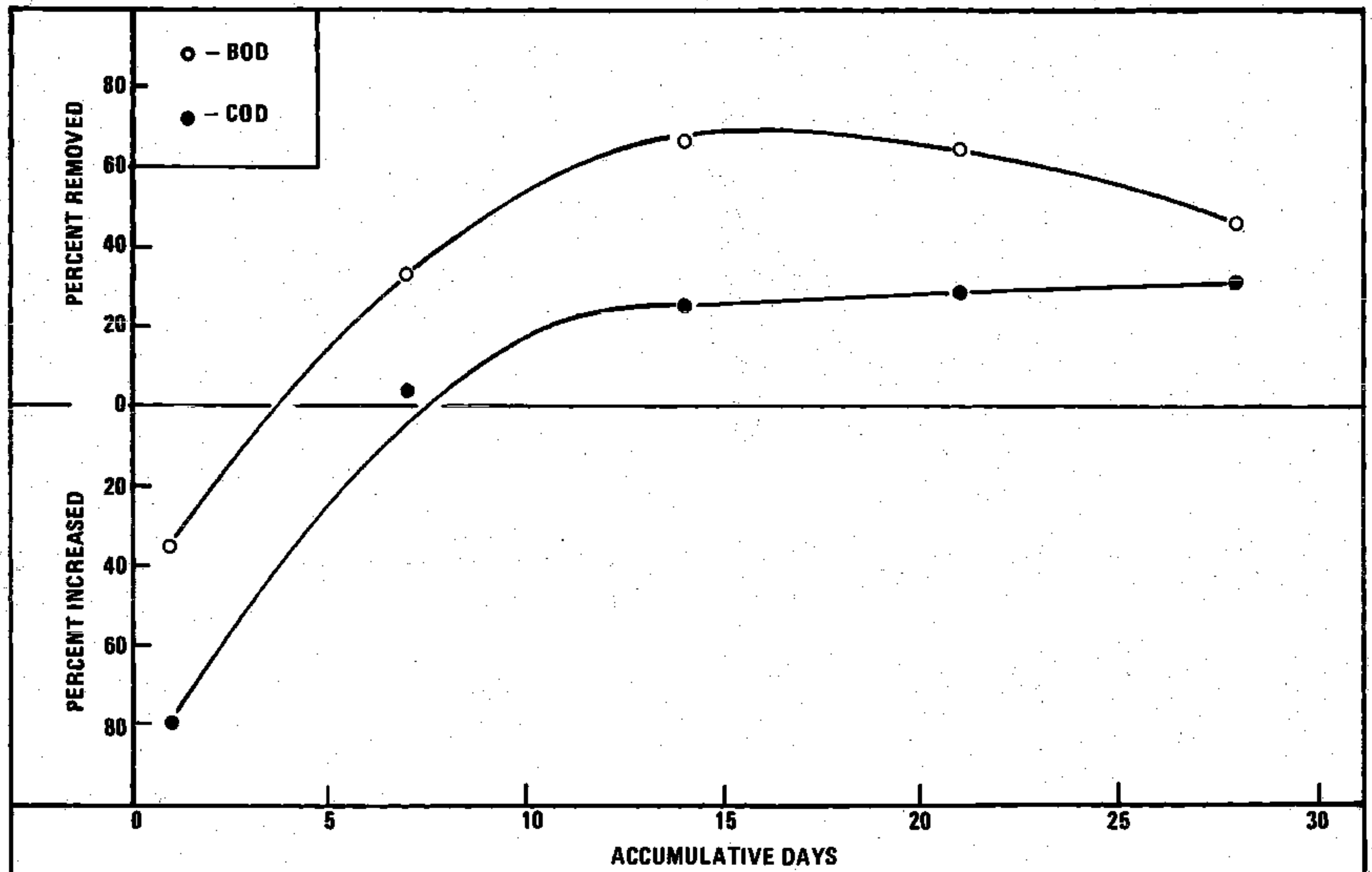

Figure 10. Effect of Time and Suspended Dosing on the Performance of Filter Number 7

Table 9. Filter Number 7, Chemical and Physical Properties of Influents and Filtrates

	Σ Days	1	3	5	7	14	21	28
pH	Influent	7.2	6.7	7.0	7.0	7.2	7.4	7.7
	Filtrate	6.1	6.4	6.8	6.9	7.2	7.4	7.2
Specific Conductance (μmhos, cm^{-1})	Influent	4100	4000	4000	3900	4700	4700	4600
	Filtrate	4100	3800	3800	3700	4400	4700	4400
Sodium Ion (PPM)	Influent	550	580	530	550	620	670	620
	Filtrate	480	530	580	550	620	670	670
Color (CCU)	Influent	900*	1160	1120	1360	520	520	570
	Filtrate	1640	1540	1120	1440	680	640	640

*Filtered twice through 0.8 μ membrane filter.

The specific conductance of the filtrate was lower than the influent for five of the seven readings taken with no change recorded for two observations.

Observed values of the sodium ion activity show a removal of 13 and 8.6 percent of this ion from the influent on the first day and third day, respectively. On the 5th day and 28th day measured values show a slight increase in this ion's concentration in the filtrate. Three other measurements show no change in the sodium ion activity.

Concentration of color bodies in the filtrate increased for six of the seven observed measurements taken, with one measurement exhibiting no change between the influent and filtrate.

Filter Number 8

This model simulated the operation of a filter where a fraction of the filtrate was recirculated and mixed with the influent. The recirculation ratio selected was 1 : 1 and is the ratio of recirculation hydraulic rate to raw waste water hydraulic rate. Hydraulic rates were as stated in Chapter III.

BOD and COD removal efficiencies associated with this model are indicated in Figure 11.

BOD removal efficiency did not exhibit appreciable change during the time interval the model was under observation. The efficiency was approximately 80 percent on the 9th day and the 42nd day of operation.

The COD curve followed a pattern similar to the BOD curve except the indicated removal efficiency was 35 percent.

Chemical and physical characteristics of the influents and filtrates are recorded in Table 10.

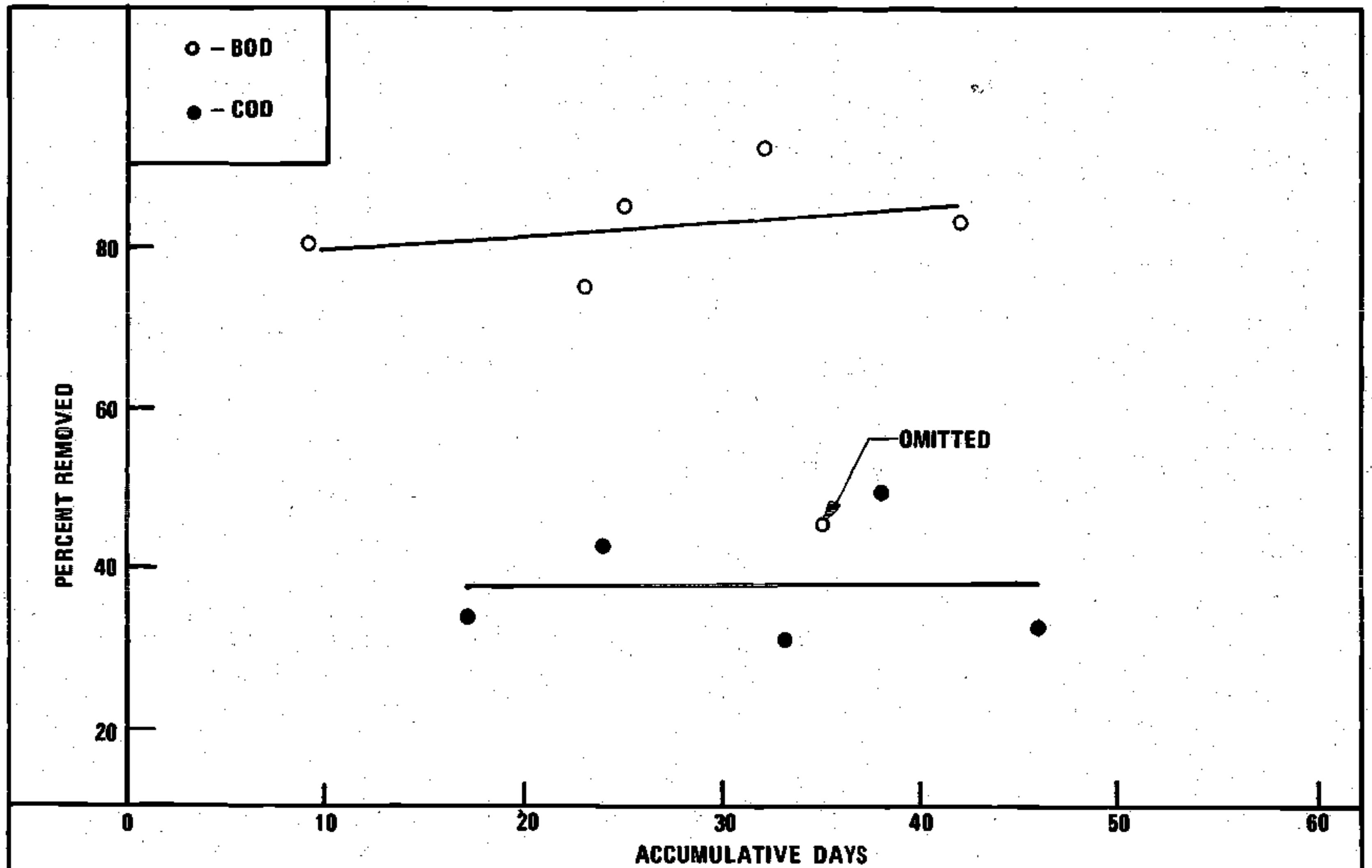

Figure 11. Effect of Time and Recirculation on the Performance of Filter Number 8

Table 10. Filter Number 8, Chemical and Physical Properties of Influents and Filtrates

pH

Σ Days	8	14	22	25	29	37	43
Influent	6.5	7.2	6.5	8.4	7.1	7.7	7.9
Filtrate	6.7	7.4	7.5	7.6	7.6	7.9	7.8

Specific Conductance (μmhos, cm^{-1})

Σ Days	8	14	22	25	29	37	43
Influent	6300	6200	6500	6600	6300	6200	6500
Filtrate	11300	7200	7200	6500	6600	6800	6500

Sodium Ion (PPM)

Σ Days	25	38
Influent	1000	990
Filtrate	1000	940

Color (CCU)

Σ Days	8	15	29	37	43	45
Influent	1560*	1170*	1590*	1710*	1890	2790
Filtrate	900*	1600*	1560*	1340*	1480	1590

*Error in procedure.

Collation of data shows that the hydrogen ion activity generally decreased when the influent was passed through the bark filter media. However, when the influent measured pH value was 7.9 and greater, the hydrogen ion activity of the filtrate increased.

Specific conductance of the filtrate increased for five observations, decreased for one, and remained unchanged for one. Collation of the data shows that the ionic activity of the filtrate decreased with time from a measured value of 11,300 μmhos, cm^{-1} on the 8th day to 6500 μmhos, cm^{-1} on the 43rd day.

Two observations were taken to measure the change in the sodium ion concentration of the influent after treatment through the filter model. These two observations were made on the 25th day and the 38th day resulting in no change and a five percent decrease, respectively.

The performance of this model indicated significant removal of color bodies from the influent. Two observations show a removal of 22 percent and 43 percent. The points in time of these observations were the 37th day and the 45th day.

<u>Composted Bark as a Filter Media</u>

This filter model study was undertaken as a special project. Instrumentation, equipment, and test procedures were the same as the other filter models. The operational procedure was the same except shredded, composted bark was used as a media instead of raw pine bark. This composted bark was purchased at a local nursery under the trade name "Tara Humus" and it is distributed by Pike Nurseries, Inc.

The limited experimental data characterizing the chemical and physical properties of the influents and filtrates are shown in Table 11.

For the two BOD removal performance values taken, the arithmetic means efficiency was 83 percent. These two points were taken near the termination of the project.

COD removed from the influent, when passed through the composted bark media was erratic for the three removal efficiencies taken. A high efficiency of 49 percent was recorded on the third day and a low of 13 percent on the 11th day.

The hydrogen ion activity in the filtrate increased for each of the four measurements taken.

Results show a significant reduction in the ionic activity in the filtrate on the first day of this filter's operation. Measured resistivity values of the two streams show a reduction of 5230 μmhos, cm^{-1} in the filtrate. The two other data points taken on the 8th and 30th days show a slight reduction in specific conductance.

There was a significant reduction in the sodium ion concentration in the filtrate on the second day of operation. Observed data indicate an 88 percent decrease. Data taken on the 24th and 30th days show an increase in the activity of this ion in the filtrate.

After eight days of operation, observed data indicate that the filter removal performance of color bodies in the influent was 71 percent and 53 percent at the end of 11 days. On the 24th day and the 30th day the concentration of color bodies in the filtrate increased.

Table 11. Filter Number 9, Chemical and Physical Properties of Influents and Filtrates

pH	Σ Days	2	8	11	30
	Influent	7.6	8.0	7.9	7.0
	Filtrate	6.2	5.1	5.3	6.0
COD (mg, l^{-1})	Σ Days	3	11	32	
	Influent	588	574	800	
	Filtrate	302	502	560	
Specific Conductance ($\mu mhos, cm^{-1}$)	Σ Days	1	8	30	
	Influent	6200	6500	3900	
	Filtrate	970	5700	3700	
Color (CCU)	Σ Days	8	11	24	30
	Influent	1440	1520	900*	1360
	Filtrate	420	725	1320	1550
BOD (mg, l^{-1})	Σ Days	24	30		
	Influent	160	135		
	Filtrate	12	36		
Sodium Ion (PPM)	Σ Days	2	24	30	
	Influent	940	550	550	
	Filtrate	115	990	580	

*Filtered twice through 0.8 μ membrane filter.

CHAPTER V

DISCUSSION OF RESULTS

Acclimatization Period

On the initial start-up of a filter model the concentration of BOD in the filtrate was greater than that in the influent. This increase in BOD concentration is attributed to the soluble organic fraction in the bark media extracted by the liquid influent. The results indicate that a four to fifteen day period was required for the filter environment to be acclimatized to all soluble biodegradable organic matter in the liquid medium so that microbial metabolism would reduce the BOD concentration of the liquid fluid.

Performance curve comparisons of filter model number 1 with filter model number 7 show that a higher loading rate required fewer days for acclimatization.

Dewatering and Purifying

The results indicate that when a fibrous kraft mill primary sludge (3.5 percent solids) was passed through simulated trickling filter models, 70 to 90 percent of the BOD in the liquid fraction of the influent was removed. This range of removal took place in a time span of approximately 40 days after an acclimatization period. A very high percent (99 percent plus) of the suspended solids in the sludge remained with the filter. A large fraction of these solids was captured at the surface of the filter face and presented a dewatered sludge containing about 18 percent solids.

The dewatered sludge reduced the flow of liquid through the filter so that periodically it had to be removed. It is not clear how the sludge could best be removed from the filter face in a full scale model. It is possible that blinding may not be as severe under more realistic conditions or perhaps the accumulated sludge mass could be mechanically removed periodically.

Coupling sludge dewatering with good BOD reduction in the waste water fraction of the sludge into one process suggests an incentive for economical consideration.

Bark Depth

Results indicate that BOD and COD removal performance does not change significantly when the bark depth is extended beyond three feet and the influent is applied at a rate of 4.59 gallons, ft^{-2}, day^{-1}.

Bark Nitrogen Concentration

As the results indicate the nitrogen concentration of the bark increased during the operational time interval of the project. This increase in bark nitrogen concentration is thought to be from the nitrogen constituent in the dead bodies of microorganisms. The increased nitrogen concentration in the lower portion of the filter is thought to be lysate (fragmented microorganisms) from the top section. The flowing liquid transports these insoluble lysates to a lower position in the filter where they could be removed by sedimentation in the boundary layer between the flowing liquid and the bark surface.

One economic consideration of a good soil amendment is a low carbon to nitrogen ratio (C/N). This low ratio is necessary or additional nitrogen must be added to the soil to offset the nitrogen temporarily lost to protoplasm of microorganisms using the organic matter as a carbon source. Allison (15) studied the decomposition of southern pine barks in soils and reported that the percent carbon in the barks studied was about 50 percent on a dry basis. Using these data, a conservative estimate of the C/N ratio of the pine bark filter media, after 50 days of filter operation, was approximately 60/1. The initial C/N ratio was approximately 178/1. Field (16) reported a C/N ratio in a completed composted bark of about 40/1. Bark that has a C/N ratio in this range, when used as a soil amendment, does not deplete the nitrogen constituent in the soil.

BOD and COD Removal Performance

Collation of the BOD and COD removal performance of filters 1 through 8 suggests that a dosing rate of 9.20 gal., ft^{-2}, day^{-1} (filter number 5) resulted in a model that is more effective from a cost-benefit position; that is, a model exhibiting a high BOD removal efficiency at a higher hydraulic loading rate when compared with the other models. Also, this model demonstrated a higher COD removal performance.

Filters with dosing rates higher than 9.20 obtained BOD removal efficiency of about 80 percent. These higher rate filters removed a greater total mass of BOD, which is an important consideration for a roughing filter.

The decline in BOD removal efficiency during the operation of filter number 7 is attributed to the higher total BOD load (both BOD extracted from bark and influent BOD) applied. As the BOD load increases the amount of biological growth in the filter bed increases. This increased microbial growth may have filled voids in the bed sufficiently to impede the passage of air into the bed that is necessary for bio-oxidation of the waste.

Color Removal

The 9.20 rate filter shows the highest color bodies removal performance (39 percent) of all the models except the 18.4 rate recirculation model (43 percent). It is not clear by which process these color bodies were removed from the liquid. Removal could have been a binary process of adsorption onto bark particles and removal by sedimentation of the bark particles in the fluid-solid boundary layer.

Based on visual observations the filtrates were freer of turbidity than the influents, indicating the filter was removing colloidal particles from the liquid medium.

Suspended Dosing

The 12 day suspended dosing period had little effect on a filter's removal efficiency of BOD from the waste stream on the first day of resumed operation. This indicates that sufficient oxygen, food, moisture, and nutrients were available at the bark surface to sustain microbial metabolism. The biodegradable constituents remaining in the bark were probably the primary microbial food source during this interval. This hypothesis indicates one possible advantage of using a non-inert filter media, such as bark.

The results show that the COD removal performance significantly deteriorated on the first day of operation following the 12 day suspended dosing period. However, after seven days of operation the removal performance equaled or significantly exceeded any previous values.

Collation of data points on the 58th day in Figures 7, 8, and 9 shows that, as the hydraulic loading rate increases, COD removal performance increases. Also, the hydrogen ion activity increases as shown by observations taken on the 61st day. No detectable pattern changes were noted in the specific conductance, sodium ion activity, or color bodies concentration.

Composted Bark Media Model

A limited number of performance observations were made during the operation of this filter model. The results clearly indicate that a shredded, composted bark used as a filter media is effective in removing BOD and COD and in substantially reducing the ionic activity, color, and sodium in a waste water stream.

Hergert et al. (17) reported results which suggest that aerobic aging in the presence of moisture (composting) converts some of the carbohydrates and extractives in bark to phenolic acids. This is a possible explanation for the increased hydrogen ion activity in the filtrate. Also, the increase in phenolic acids would tend to increase the ion exchange capacity of the bark. This extra ion exchange capacity coupled with the increased surface area of the composted bark accounts for the improved performance over raw bark in BOD, COD, color, sodium, and ion removal.

The time interval in which the media is effective in removing color and sodium is limited to about 11 days. At the end of this period these constituents were released back into the liquid medium.

CHAPTER VI

CONCLUSIONS

1. Pine bark is an effective filter for removing solids in a kraft pulp and paper mill primary sludge, removing over 99 percent of the settleable solids.

2. Primary sludge can be dewatered by a pine bark filter to approximately 18 percent solids.

3. From 70 to 90 percent of the BOD in the liquid fraction of a pulp and paper mill sludge is removed by a pine bark media trickling filter.

4. At a 4.59 gallons, ft^{-2}, day^{-1} dosing rate up to 40 percent of the COD in the liquid fraction of the sludge is removed when passed through a pine bark media trickling filter.

5. The BOD and COD removal efficiency of a pine bark media trickling filter does not significantly change after passing through approximately three feet of the bark media.

6. Pine bark is an affective trickling filter media for treating a kraft bleach plant waste water, removing up to 90 percent of the BOD and 40 percent of the COD.

7. The optimum dosing rate for a single pass pine bark media trickling filter is approximately 9.20 gallons, ft^{-2}, day^{-1}.

8. Significant amounts of sodium and color are removed by passing a kraft bleach plant waste water through a trickling filter with composted

bark as the filter media.

9. The nitrogen content of the pine bark media is significantly increased after use as a trickling filter media.

10. Four to 15 days is required for acclimatization when pine bark is used as a filter media, with higher loading rates requiring shorter acclimatization times.

11. Suspended dosing has little effect on a pine bark media trickling filter.

12. Single pass bark media trickling filters were as effective in removing BOD and COD as one and one-half pass trickling filters.

CHAPTER VII

RECOMMENDATIONS

1. Installation, at a pulp mill, of a prototype filter model to treat a primary sludge should be encourage. The purpose of the project would be to determine the extent of filter face blinding and, if necessary, to develop methods to aid the penetration of the solids into the bark pile. Should blinding prove inevitable, an economical means of removing the dewatered sludge from the filter surface should be developed.

2. At the termination of the prototype project, the composted bark could be used in a horticultural project to investigate its value as a soil amendment.

3. A bark media roughing trickling filter project, with a bark depth of six feet or greater, should be built to examine biochemical, chemical, and physical properties of the liquid and bark at various filter depths over an extended time interval. This type or project could add new dimensions to composting rates and mechanical and chemical interaction between the liquid and solid media.

4. Additional research using a composed bark as the trickling filter media should be conducted.

APPENDIX

Table 12. Primary Sludge Project, BOD and COD Influent and Filtrate Data (mg, l^{-1})

	Σ Days	9	16	23	25	30	36	42	45	50
BOD	Influent	222	---*	325	375	270				
	Filter No. 1	400	---*	65	40	35	29	--*	--*	17
	Filter No. 2	120	---*	65	40	25	22	21		19
	Filter No. 3	83	---*	63	43	39	13	26	--*	--*

	Σ Days	10	17	24	31	39	46
COD	Influent	---*	737	1368	1237	506	956
	Filter No. 1	---*	1035	1180	1452	1681	1275
	Filter No. 2	---*	956	1062	1093	922	781
	Filter No. 3	---*	753	874	705	628	534

*Error in procedure.

Arithmetic mean of influent BOD measured values -- 298.

Arithmetic mean of influent COD measured values -- 961.

Table 13. Bleach Plant Waste Water Project, BOD and COD Influent and Filtrate Data (mg, l^{-1})

	Σ Days	9	16	23	25	32	36	42	45	59	65
	Influent	200	--*	250	230	450	108	171	--*	160	135
	Filter No. 4	70	--*	100	33	27	17	3	--*	23	11
	Filter No. 5	40	--*	100	30	30	19	6	--*	30	9
BOD	Filter No. 6	60	--*	80	60	69	50	69	--*	53	9
	Filter No. 8	35	--*	55	33	45	51	27			
	Σ Days	1	7	14	21	28					
	Influent	160	135	159	144	84					
	Filter No. 7	218	90	53	50	45					
	Σ Days	10	17	24	33	38	46	59	65		
	Influent	---*	941	1053	784	987	877	670	800		
	Filter No. 4	---*	895	848	--*	582	685	1110	364		
	Filter No. 5	---*	565	541	560	420	582	928	606		
COD	Filter No. 6	---*	737	643	613	645	598	639	323		
	Filter No. 8	---*	596	541	512	436	566				
	Σ Days	1	7	14	21	28					
	Influent	670	800	785	753	722					
	Filter No. 7	1200	776	586	543	501					

*Error in procedure.

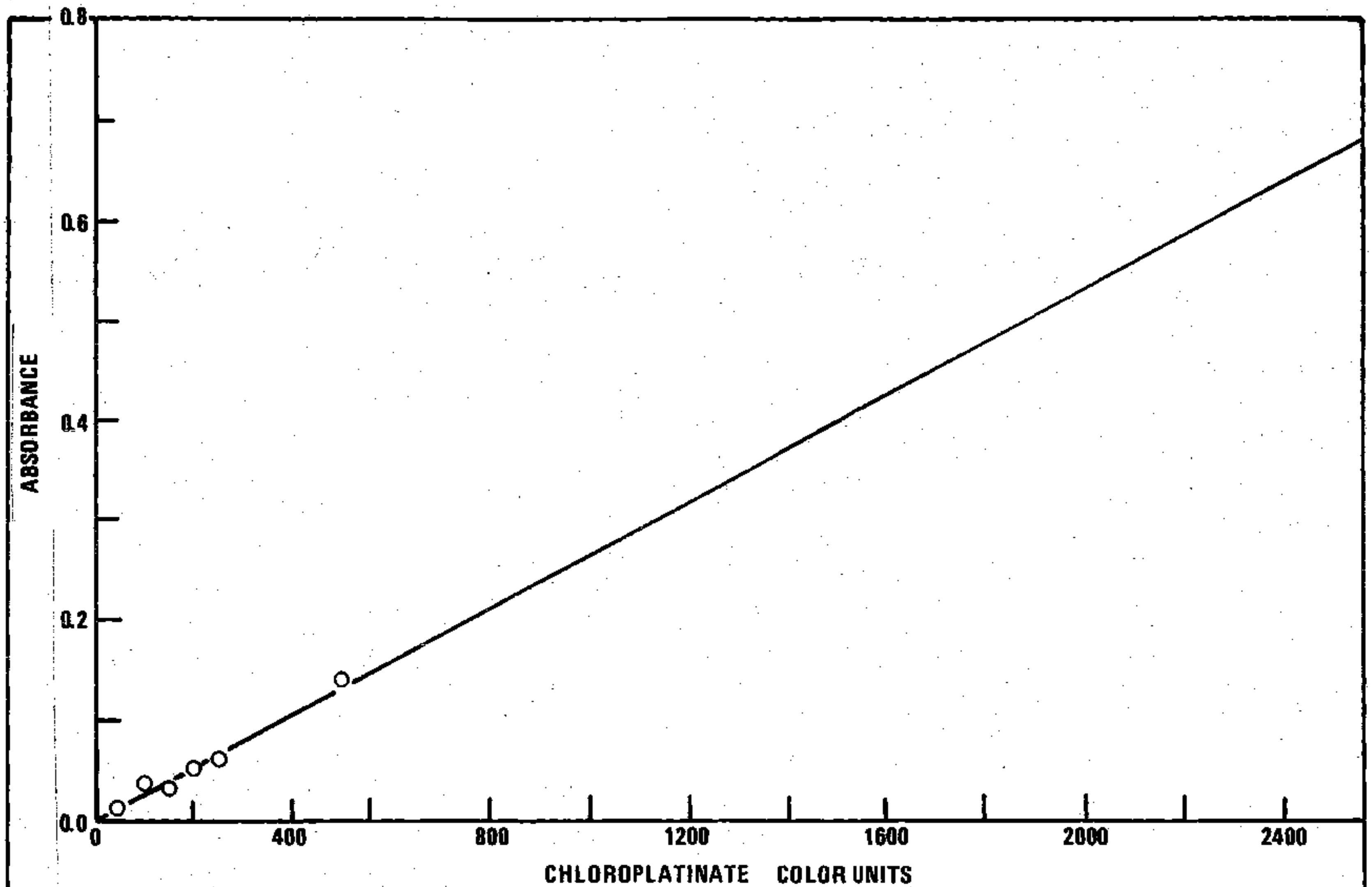

Figure 12. Working Calibration Curve to Determine Chloroplatinate Color Units (CCU)

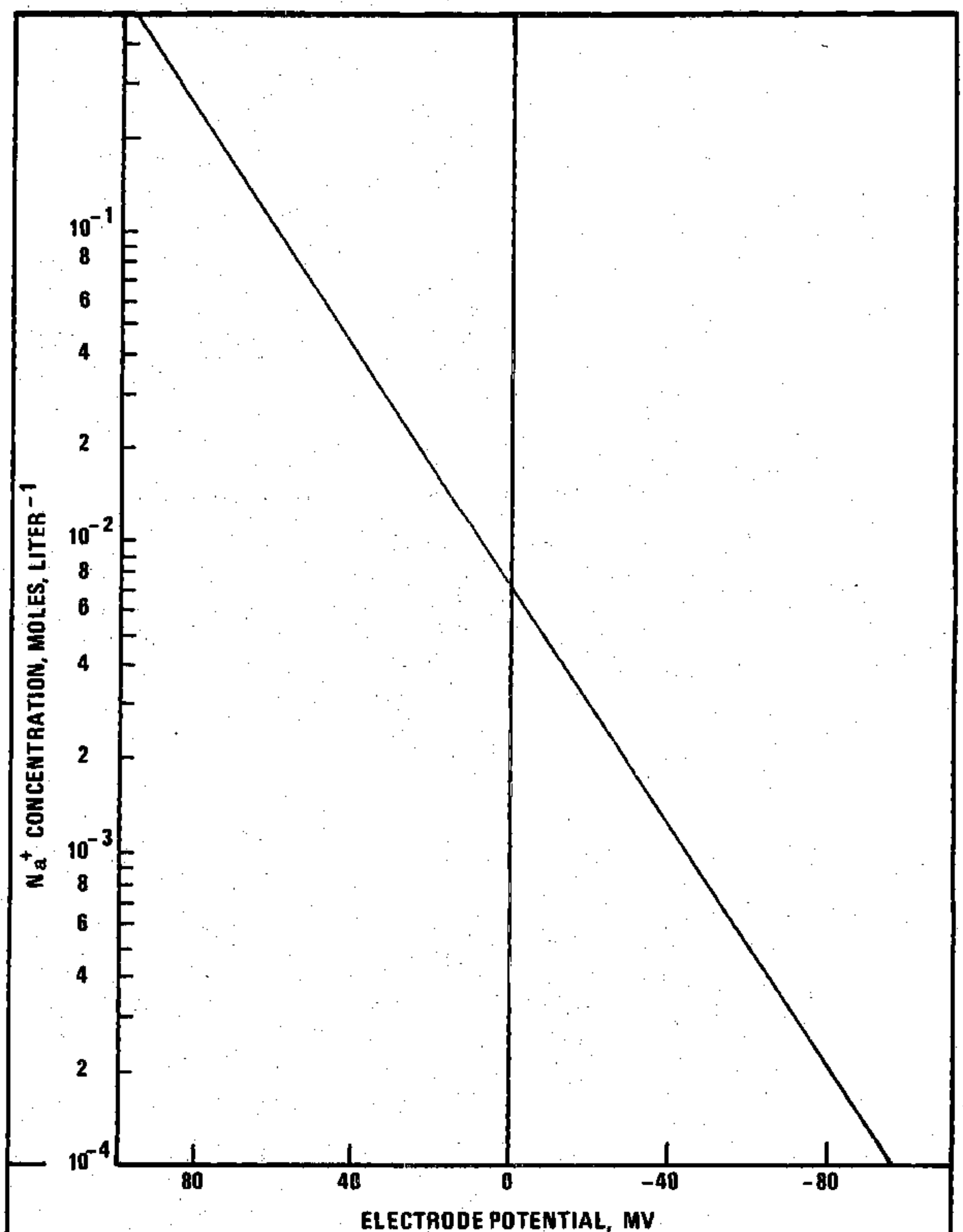

Figure 13. Working Calibration Curve Using Sodium Selective Electrode

Table 14. Data for Least Squares Fit

Equation: $y = b_0 + b_1x^1 + bx^2, \ldots, b_nx^n$

σ^2 = Variance σ = Standard Deviation

Filter Number	BOD		COD	
1	n	4	n	2
	b_0	-255	b_0	251
	b_1	34.4	b_1	- 11.7
	b_2	- 1.26	b_2	0.16
	b_3	0.02	σ^2	126
	b_4	- 0.00	σ	11.2
	σ^2	1.82		
	σ	1.35		
2	n	2	n	2
	b_0	38.9	b_0	65.0
	b_1	2.56	b_1	- 5.51
	b_2	- 0.029	b_2	0.098
	σ^2	4.93	σ^2	5.85
	σ	2.22	σ	2.42
3	n	2	n	1
	b_0	61.8	b_0	- 2.88
	b_1	1.12	b_1	0.964
	b_2	- 0.009	σ^2	41.1
	σ^2	8.67	σ	6.41
	σ	2.95		
4	n	1	n	1
	b_0	51.8	b_0	- 1.19
	b_1	1.05	b_1	0.74
	σ^2	73.5	σ^2	9.60
	σ	8.58	σ	92

Table 14. Continued

Filter Number	BOD		COD	
5	n	1	n	1
	b_0	67.1	b_0	45.3
	b_1	0.58	b_1	- 0.11
	σ^2	104	σ^2	
	σ	10.2	σ	
6	n	2	n	2
	b_0	58.3	b_0	12.2
	b_1	1.51	b_1	1.03
	b_2	- 0.04	b_2	- 0.01
	σ^2	69.5	σ^2	42.5
	σ	8.33	σ	6.52
7	n	3	n	4
	b_0	- 52.1	b_0	- 103
	b_1	16.7	b_1	25.9
	b_2	- 0.70	b_2	- 1.95
	b_3	0.01	b_3	0.07
	σ^2	0.05	b_4	- 0.00
	σ	0.22	σ^2	1.52×10^{-12}
			σ	0.123×10^{-6}
8	n	1	n	1
	b_0	80.5	b_0	41.5
	b_1	0.14	b_1	0.02
	σ^2	13.2	σ^2	44.4
	σ	3.63	σ	6.67

BIBLIOGRAPHY

1. Gehm, Harry W., and George W. Goue, Kraft Mill Waste Treatment in the United States--A Status Report, National Council Technical Bulletin No. 221 (1968)

2. Britt, Kenneth W., Pulp and Paper Technology, Second Edition, Van Nostrand Reinhold Company (1970)

3. Libby, Earl C., Pulp and Paper Science and Technology, Vol. 1, p. 139, McGraw-Hill Book Co. (1962)

4. Ivory, E. P., and Field, P., Utilizing Bark at a Medium-Size Mill, Forest Prod. J., April (1959)

5. Burton, R. E., Bark as a Trickling Filter Media, Forest Prod. J., Vol. 9, No. 4, p. 19A, April (1959)

6. Adams, R., Composting Tree Bark with Sewage, Compost Science, Vol. 12, No. 3, p. 24, May-June (1971)

7. Cropsey, Myron G., and Wesivig, Paul H., Douglas-Fir Bark as a Trickling Filter Medium for Animal Waste Disposal Systems, Oregon State University, Agr. Exp. Station, Corvallis, Oregon

8. Lightsey, G. R., Quality of Seepage and Run-off Water from Foley By-Products Storage Area, Tech. Div. Report 3080, The Buckeye Cellulose Corp., July (1973), unpublished

9. Lightsey, G. R., Disposal of Prehydrolysate by Land Irrigation and Bark Composting, Tech. Div. Report 3076, The Buckeye Cellulose Corp., July (1973), unpublished

10. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York (1971)

11. National Council of the Paper Industry for Air and Stream Improvement, Incorporated, An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color, Tech. Bulletin No. 253, December (1971)

12. Fisher Scientific Company, Sodium Ion Selective Electrode, Instructions, E-15, Catalog No. 13-639-20

13. Environmental Protection Agency, Methods for Pulp and Paper Mill Sludge Utilization and Disposal, EPA-R2-73-232, p. 3 (1973)

BIBLIOGRAPHY (Concluded)

14. Allison, F. E., Decomposition of Wood and Bark Sawdusts in Soil, Nitrogen Requirements and Effects on Plants, USDA Agr. Res. Serv., Tech. Bulletin 1332 (1965)

15. Field, P., Residues from the Sawmills--Making Smoke or Profit?, Forest Prod. J., 8(11): 27A-30A (1958)

16. Hergert, H. L., Ban Blaricom, L. E., Steinberg, J. C., and Gray, K. R., Isolation and Properties of Dispersants from Western Hemlock Bark, Forest Prod. J., 15(11): 485-491 (1965)